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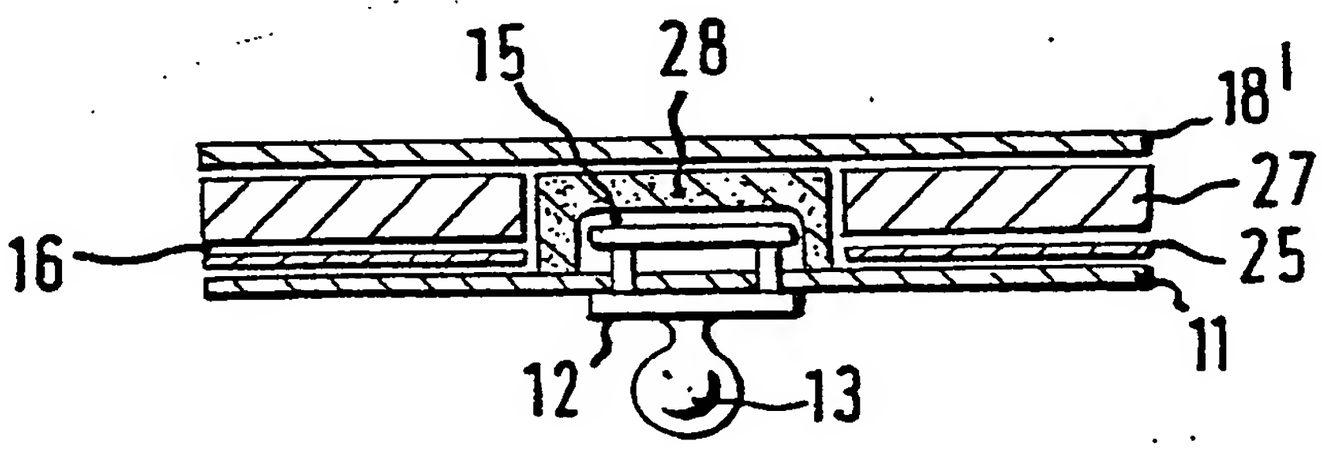

(57) Abstract

Formable polymer composition having electrically-conductive properties. The composition in its broadest aspect comprises a formable polymeric material having dispersed therein an electrically-conductive material in particulate form comprising metal or metal coated particles, the conductive material being present in an amount to provide an overall specific conductivity in the composition of at least about 2 mho cm^{-1}. In one preferred aspect the composition includes one or more components to provide a composition having contact adhesive properties which can be used to produce a transducer. Such a transducer comprises a backing member (11) through which is mounted an electrically-conductive contact (12) whereby an electrical lead can be connected to one part of the contact at the rear (14) of the backing member and the contact provides an unbroken electrical path through the backing member to a portion of said electrically-conductive adhesive composition (28) forming at least part of an adhesive layer disposed on the front of the backing member whereby the front of the transducer may be adhered to the skin. The above transducer device is useful in e.c.g. measurement applications.

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FORMABLE POLYMER COMPOSITION

The present invention relates to a formable polymer composition, in particular a composition which has electrically-conductive properties, those properties being retained even after forming.

There are many situations in which an electrically-conductive polymeric material which is formable might find ready application. This is especially true in the medical field where an electrically-conductive formable polymeric material which is also contact-adhesive to the human skin would find many applications. For example, such a material would find application in the production of electrocardialogical monitoring transducers and cardiac stimulation devices, both commonly known as "electrodes".

According to the present invention in its broadest aspect there is provided a formable polymer composition, which composition comprises a formable polymeric material having dispersed therein an electrically-conductive material in particulate form comprising metal or metal-coated particles, the conductive material being present in an amount to provide an overall specific conductivity in the composition of at least about 2 mho cm^{-1}.

We have found quite surprisingly that a wide range of formable polymeric materials can be formulated with an electrically-conductive material comprising metal or metal-coated substrate particles and in an amount to provide an overall specific conductivity in the composition which makes it truly electrically-conductive, while at the same time remaining formable. That is to say compositions can be formulated in which a formable polymeric base material retains a significant and meaningful proportion of its processing characteristics, so as to make the compositions formable in various ways, for example, by moulding, extrusion or other shaping techniques, while at the same time affording true electrical conductivity.

In the compositions of the invention, the electrically-conductive material in particulate form may comprise a metal as such, for example, lead, copper, iron, steel, platinum, gold or silver. Alternatively,

and especially for low current applications, the electrically-conductive material may comprise substrate particles coated with a film of metal. Thus, silver which is suitable for medical applications can be prepared as described below in a relatively cheap particulate form coated on substrate particles and as such is especially preferred for low current applications.

In the composition of the invention, metal or metal-coated particles are randomly dispersed throughout a non-conductive formable polymeric matrix in a proportion which exceeds that of the critical percolation volume indicated by percolation theory as it applies to the unstructured case of non-interpenetrating bodies of specified shape and size distribution. In excess of this critical percolation proportion, it is inevitable that a sufficient number of the conducting particles are in contact with each other so as to provide random conducting pathways throughout the polymeric material, no matter what shape ultimately it is made to adopt.

Since the random electrically-conducting pathways occur as a result of surface contact between the randomly dispersed particles of conductive material, considerable cost savings can be effected, where low current applications are involved, by using non-conducting substrate particles bearing a thin coating or film of a metal. In the case of medical devices placed in contact with the skin, they preferably include a metallic conductor which is non-corroding, non-corrosive, non-toxic and which neither exhibits nor affords any adverse side effects when placed in close contact with the human skin for extended periods of time. In that respect metallic silver is a preferred conductive material and in the case of silver the cost reduction obtained by depositing a thin coating of silver on a suitable substrate is substantial.

As is clearly evident from percolation theory, and from the theory of packing spheres or other bodies in space, further (if smaller) cost reductions can be obtained by the use of uniform or relatively uniform spherical particles. This is especially true if they are graded to have a narrow spectrum of particle size, since this leads to a lower critical percolation volume.

In that respect, the requirements of the present invention for low current applications maybe met by providing a substrate which comprises small glass spheres (ballotini) which are available in medically approved grades. The spheres can easily be coated with a thin layer of silver, typically a film having a thickness of about a few Angstrom units, by the well known chemical reduction process using a silver salt, for example, silver nitrate and invert sugar. This is the basis of the "silver mirror" test used in classical chemical analysis. Alternatively, the spheres may be of metal-coated e.g. silver-coated, plastics material.

As mentioned above the conductive material must be present in the formable plastics composition of the invention in an amount to provide an overall specific conductivity of at least about 2 mho cm^{-1}. Preferably, however, the conductive material is present in an amount to provide an overall specific conductivity of from about 10 mho cm^{-1} to about 100 mho cm^{-1}.

The proportion of electrically-conductive particles in the overall polymeric matrix necessary to achieve the above-mentioned levels of overall specific conductivity is highly dependent on the shape and distribution of shapes of the particles and on their size distribution. However, expressed on a volume basis that proportion for any given shape and distribution is essentially independent of the kind of conductive material employed, i.e. which metal is used, and whether or not metal particles or metal-coated particles are employed. In the case of spheres of narrow diameter distribution, preferably silver-coated glass spheres, they may typically be present in an amount in excess of about 35% by volume of the total volume of the composition to provide the necessary conductivity, with an upper limit of about 68% by volume for randomly packed spheres after shaking to maximise packing or about 74% by volume for spheres that are "close-packed", i.e. packed in the most efficient and regular manner. Typically, the upper limit to avoid excessive loss of polymer properties will be about 60% by volume, preferably about 55% by volume.

It is to be understood, of course, that the particulate form chosen need not be spherical. Thus, while silver-coated glass spheres or steel spheres are

particularly useful in the preparation of formable contact adhesive compositions as described below, the incorporation of spherical particles can adversely affect the tensile properties of polymeric materials. Accordingly, where good tensile properties are important the particulate form chosen preferably will be an elongate form with a high length to diameter ratio such as rods or fibres. Again, percolation theory is sufficiently advanced for randomly oriented cylinders of uniform length and a high length to diameter ratio, i.e. rods, to provide accurate predictions from theory of the levels of rod-like or fibre particles necessary to achieve the above-stated specific conductivity.

In the case of elongate particles it is likely that electrical conductivity in a composition which has been subjected to forming by a flow process (e.g. extrusion) will be anisotropic. Such anisotropy may be advantageous for certain applications such as conductive cables. However, if this property is not required it can be reduced or eliminated by the incorporation of a (usually small) proportion of spherical particles in addition to the fibre or other rod-like particles.

The polymeric material of the formable composition of the invention may be selected from a wide variety of formable polymeric materials. Thus, the polymeric material may be a thermoplastics material or a thermo- or cold-setting material, of which preferred thermoplastics materials are, for example, polyvinyl compounds, e.g. polyvinylchlorides; polyalkenes, e.g. polyethylenes, polypropylenes and polyisobutenes; polyacrylates; polymethacrylates; and polyamides e.g. nylon, and of which preferred thermo- or cold-setting materials are, for example, epoxy resins and silicones e.g. silicone rubbers.

In the case of the specific medical applications mentioned below, the composition of the invention preferably includes one or more components which provide a composition having contact- or pressure-sensitive adhesive properties. Preferably also, the components of the composition should be selected so as to provide a hypoallergenic composition, especially in the case of any application where the composition may remain in contact with the skin for a long period of time.

A preferred composition for use in applications

involving contact with the human skin is based on a polyisobutene mixed with one or more phase structure, flow and/or moisture permeability modifiers, for example, low molecular weight polyalkenes, e.g. polyethylene, or hydroxyalkyl celluloses, e.g. hydroxymethylcellulose. In such a composition the polyisobutene typically has a viscosity average molecular weight in the range of from about 40,000 to about 100,000.

The invention also includes an electrically-conductive device for medical purposes, which device comprises one or more formed portions of a composition in accordance with the invention, if desired supported on a substrate structure.

In one embodiment, the device of the invention is a transducer suitable for use in electrocardialogical applications in place of the so-called "electrodes" of the prior art. In that embodiment the substrate structure comprises a backing member through which is mounted an electrically-conductive contact whereby an electrical lead can be connected to one part of the contact at the rear of the backing member and the contact provides an unbroken electrical path through the backing member to a portion of an electrically-conductive adhesive composition in accordance with the invention forming at least part of an adhesive layer disposed on the front of the backing member whereby the front of the transducer may be adhered to the skin.

Preferably, the electrically-conductive contact is a stud compatible with existing e.c.g. leads which provides a means of connecting the leads to the transducer. Such a stud may be formed of metal or of a formable composition in accordance with the invention which can provide a suitably formed rigid stud e.g. a composition based on nylon or polypropylene. Preferably also, the contact is mounted at or about the centre of the backing member and, in order to avoid uncomfortable corners, the backing member is preferably a disc. With such a disc the front surface of the backing member preferably bears an annulus of non-conducting contact adhesive material surrounding a central portion or plug of said electrically-conductive adhesive composition. Preferably, the annulus is formed of a hypoallergenic pressure-sensitive skin adhesive material, for example,

a foamed layer having an adhesive coating e.g. of an acrylic composition, on its upper and lower faces, such as has been found suitable for ostomy applications.

Additionally, in another embodiment of the invention, the device may be a multiple contact transducer for e.c.g. applications and comprising an array of electrically-conductive portions carried on an insulating backing member, each portion being in electrical contact with an isolated terminal, and at least one portion comprising an electrically-conductive adhesive composition according to the invention.

In this second embodiment, the electrically-conductive portions preferably are disposed on the backing member in an arcuate array for attaching to a patient's chest around the heart. Preferably also there are at least three electrically-conductive portions.

As described in more detail below, one form of transducer as first defined above can be manufactured by a method which comprises:

(a) forming a sheet of a laminate comprising a layer of a conductive and adhesive composition according to the invention sandwiched between two release layers,

(b) sub-dividing the laminate into transducer elements, preferably elements which are disc-shaped,

(c) removing one release layer, and

(d) adhering each element via its exposed adhesive face to a backing element, preferably of the same shape, and including an electrically-conductive contact which provides an unbroken electrical path through the backing member to the conductive composition.

Alternatively, transducers of both embodiments may be produced by a method which comprises:

(i) forming a sheet of laminate comprising a layer of non-conducting contact adhesive composition, such as is presently used in ostomy, sandwiched between a release layer and a supporting layer,

(ii) sub-dividing the laminate into transducer elements,

(iii) providing at least one aperture through each element,

(iv) adhering each element via its supporting layer to a backing element, preferably of the same shape, and including an electrically-conductive contact which provides an unbroken electrical path through the backing

member to the or each aperture,
(v) removing the release layer,
(vi) filling at least one aperture with a portion of a conductive and adhesive composition according to the invention, and
(vii) covering the front adhesive face with a release layer.

In one embodiment as described below, the electrode elements are discs and the apertures are essentially round in plan. In another embodiment as described below the electrode elements are horse-shoe shaped, and preferably at least three e.g. six, apertures are provided.

In providing an electrically-conductive adhesive composition in accordance with the invention, generally for applications as described immediately above, variable conductivity characteristics can be encountered due to the electrically insulating nature of dead skin carried on the body surface. This can be avoided simply by first preparing the skin surface e.g. by lightly abrading with emery paper, or with a pumice stone or the like to remove dead skin. Such preparation, however, even though it is simple and quick may not be desirable in certain circumstances, and in any event relies on a nurse or other operative involved to carry out the preparation.

Accordingly, in order to avoid the need for any skin preparation, in a preferred aspect the composition according to the invention includes an additive to reduce contact resistance with the skin when applied to unprepared skin, that is skin from which the keratin (dead skin) layer has not been removed by abrasion or the like.

Preferably, such an additive is one which provides an aqueous medium within the composition to provide the necessary electrical continuity through the keratin layer. Thus, the composition preferably includes an additive comprising a mixture of:

1. Water,
2. A hygroscopic agent such as glycerine or glycerol, and
3. A thickening agent, for example, carboxymethyl-cellulose,

which mixture may be used in an amount of, for example,

from about 1% to about 5% by weight of the total composition.

In preparing a composition containing an additive to reduce skin contact resistance, it is convenient to prepare a first mixture comprising additive and electrically-conductive material, and a second mixture comprising polymer and electrically-conductive material, those mixtures then being blended to form the final composition. When that method is employed, preferred ranges of the various components for the first mixture are:

1. A ratio of hygroscopic agent e.g. glycerol, to water of from about 20:80 to about 80:20 by weight,
2. A proportion of thickening agent e.g. CMC, to hygroscopic agent/water mixture of from about 2% to about 10% by weight, and
3. A percentage of electrically-conductive material, e.g. silver-coated glass spheres, in the overall mixture of from about 70% to about 80% by weight.

Generally, the overall composition will include no more than about 20% by weight of such a first mixture including said additive since the use of more than about 20% by weight could result in a composition that is both too soft and which could leave a heavy residual deposit on the skin when the transducer is removed after use. Preferably, the upper limit for the first mixture is about 15% by weight based on the total weight of the composition.

It is believed that by the use of the above-described additive, "droplets" of aqueous material (filled with conducting spheres) are dispersed throughout the polymer and, on contact with the skin, sufficient water is transferred to the skin to reduce its electrical resistance. The process is aided by sodium ions from the CMC which are also in this phase and further relies on osmotic processes taking place at the skin (keratin) layer. The CMC also acts as a thickening agent to assist in the dispersion of the spheres in the first mixture and in the distribution and stability of droplets of the first mixture throughout the final composition. Furthermore, loss of moisture from the transducer is prevented by virtue of the hygroscopic nature of glycerol.

The following Examples illustrate specific compositions in accordance with one aspect of the invention, namely the provision of an electrically-conductive hypoallergenic skin adhesive composition.

Example 1

A composition in accordance with the invention was formulated as follows:

Component	% by weight on the total composition
Silver-coated glass spheres prepared as described below	72
Polyisobutene (Viscosity average molecular weight about 50,000)	28

The above electrically-conductive hypoallergenic adhesive was prepared from the above-identified components in the above amounts by mixing the coated spheres with the polymeric component in a Z-blade high shear mixer for about 20 minutes at a mixing speed of about 200 r.p.m.

The silver-coated glass spheres used in the above composition were prepared according to the following procedure:

1. Preparation of solutions:

There are four solutions required:

A) An aqueous solution of silver nitrate, containing 60 g of nitrate per litre of solution (for stability reasons this should be kept in a dark glass flask with a stone stopper).

B) An aqueous solution of ammonium nitrate, containing 90 g of nitrate per litre (flask with stone stopper).

C) An aqueous solution of potassium hydroxide, containing 150 g of KOH per litre. If desired this solution can be replaced by an aqueous solution of sodium bicarbonate containing 105 g of sodium bicarbonate per litre (in a flask with rubber stopper).

D) A saccharose solution containing:
100 g of table sugar (saccharose)
5 g of tartaric acid
150 ml of 90% ethyl alcohol
and sufficient distilled water to obtain 1 litre of solution.

Method for preparing Solution D:

Dissolve the sugar and tartaric acid in a little distilled water, bring to the boil and heat gently for 10 to 15 minutes in order to invert the sugar. Cool, by adding a little more water, before adding the alcohol which will conserve the inverted sugar. Finally, add the remaining water to obtain 1 litre. This solution has to age for at least one week and further improves with age. On the other hand solutions B and C give unreliable results after ageing, and should therefore be prepared freshly for use.

2. Cleaning the spheres and surface preparation:

The adhesion and strength of the silver coating depends very much on the cleaning of the sphere surfaces. It is very difficult to clean glass perfectly, and variations in the quality of the surface, type of glass etc. can give very different results. Experience shows, however, that rough cleaning of the surfaces is usually sufficient for coating.

Cleaning is effected by using fuming nitric acid. With this treatment any silver coating present is destroyed, and where a first coating is present the spheres should be rinsed with distilled water and again cleaned with acid.

For a first cleaning, however, a single cleaning in acid followed by extended rinsing and standing in distilled water may be sufficient. As an alternative sulphur-chromic acid may be used for cleaning: this is very effective hot, but is not easy to use.

3. Method of silver coating:

The coating operation is performed at ambient temperatures using a shallow tray into which the glass spheres are placed. The glass spheres used are glass ballotini of 0 to 20 microns diameter, made of soda glass, and obtained from English Glass, cheaper leaded glass being avoided for toxicological reasons. Since this grade of ballotini contains traces of ferrous metallic contamination, this is first removed by agitating a slurry of the spheres in water using a magnetic stirrer on which the traces of metallic contamination collect as a black metallic powder deposit. Removal of this contamination is necessary since the contaminant interferes to some exent with the

silver coating process described below.

Into a separate container there is poured a volume of solution A approximately equal to one-third the volume, V, of liquid that is necessary to cover the spheres in the tray. Next, the same volume (V/3) of each of solution B and then solution C are added progressively with rapid stirring. In principle, the last drops of solution C should cause the solution to become cloudy. If the solution remains clear then a few drops more of solution C are added. Alternatively, if the mixture becomes cloudy earlier, then the addition of solution C should be terminated.

The mixture of volume V thus obtained, is poured onto the layer of spheres in the tray. Then a volume of the reduction solution D equal to one-third of the volume of solution A used above is added. The reaction begins immediately, the liquid becomes cloudy and turns black, and the whole should be stirred slowly to obtain a uniform coating. After 2 minutes the tray begins to develop a metallic gleam, but it is necessary to wait for some time after that before the spheres are removed. The end of the reaction is indicated by seeing the mixture become clear with dark particles floating on the surface. The spheres may now be removed, rinsed first in water then in alcohol and dried as quickly as possible. The coating operation is then complete.

If the coating is the first coating applied to the spheres, it is best to repeat the operation again after first removing the silver coating with fuming nitric acid as described for step 2 above. Experience shows that a subsequent silver coating forms a much more adherent layer than the first. Similarly, if something goes wrong or if the coating formed appears to be poor then the operation should be repeated again.

It will be understood, of course, that

(i) any other closely fractionated range grade of glass spheres may be used in place of the 0 - 20 micron grade, and other ranges are available from English Glass;

(ii) in particular, a higher average size cut may be more advantageous in some applications, and

(iii) the glass sphere grade used (0 - 20 microns) is in any event necessarily subjected to further fractionation by the above processing since a slower

settling fraction comprising finer particles is discarded whenever the spheres are separated from associated liquid e.g. when they are removed from the tray. This in fact improves matters insofar as a narrower distribution is effectively produced, which means a lower critical percolation volume of spheres and greater preservation of the polymer matrix properties.

Example 2

Another composition in accordance with the invention was formulated as follows:

Component	% by weight of the total composition
Silver-coated glass spheres prepared as described above	70
*Polyisobutene (Viscosity average molecular weight about 80,000)	10
*Polyisobutene (Viscosity average molecular weight about 50,000)	11
**Carboxymethyl cellulose (M.W. about 550,000, high viscosity, fine particle, food grade)	6
***Low molecular weight polyethylene	3

*As sold by B.A.S.F. under the trade name Oppanol.
** Carboxymethyl cellulose, Hercules Chemicals, Blanose Cellulose Gum of which grade CMC 7HXF is appropriate.
***Low molecular weight polyethylene, A-C Polyethylene from Allied Chemicals of which grade 617A is suitable.

The above electrically-conductive hypoallergenic adhesive composition was prepared by pre-mixing all of the polymer components in the above amounts in a high shear Z-blade mixer at about 100°C for about 10 minutes and then, while continuing to mix, by slowly adding the silver-coated glass spheres at a rate slow enough to avoid the paste becoming dry in appearance.

Example 3

A further composition in accordance with the invention including components to promote electrical conductivity contact at the skin (keratin) interface was formulated as follows:

A first mixture (Mixture A) was prepared according to the formulation:

Component	% by weight of the total composition
Glycerol (B.P. grade, ex. BDH)	12.25
Water (distilled)	11.5
Carboxymethylcellulose (Hercules CMC 7HXF)	1.25
Silver-coated glass spheres	75.00
	100.00

by stirring together the glycerol and water until homogeneous, then adding the carboxymethyl cellulose slowly while stirring rapidly. The mixture becomes gel-like and should be mixed thoroughly before being covered and allowed to stand overnight. This causes the CMC to swell and dissolve to result in a highly viscous, transparent gel material. That gel was well mixed and then the silver balls added slowly while stirring, and the whole mixed thoroughly.

A second mixture (Mixture B) was also prepared according to the formulation:

Component	% by weight of the total composition
Polyisobutene (Viscosity average molecular weight about 50,000 as used in Example 2)	25
Silver-coated glass spheres	75
	100

by mixing the heated polyisobutene with the silver balls as described in Example 2 above.

Mixture B was then cooled to below about 50°C, and Mixture A was added slowly in small portions while "kneading" the whole, in a proportion of 13% by weight of Mixture A to 87% by weight of Mixture B. On completion of the mixing and kneading, the final mixture was cooled and checked for electrical conductivity, when it was then ready for use in forming the conductive skin adhesive portion of a transducer as described below.

The invention will now be further described by way of Example with reference to the accompanying drawings in which:

Figure 1 shows a cross-section through a known e.c.g. "electrode",

Figure 2 shows a cross-section through one form of e.c.g. transducer in accordance with the invention,

Figure 3 shows a cross-section through another form of e.c.g. transducer in accordance with the invention, and

Figure 4 shows a plan view from below of a multiple contact e.c.g. transducer in accordance with the invention.

Referring to the drawings, current e.c.g. "electrodes" are almost invariably constructed using the principle of a silver/silver chloride voltaic cell to obtain maximum electrical contact with the skin at suitable monitoring locations. Universally, they take the form shown in Figure 1, in which the "electrode" structure comprises a flexible plastics disc-shaped backing member 11, typically comprising plasticised polyvinylchloride. The backing member 11 has mounted thereon through its centre a metal "press stud" contact 12, which includes a stud portion 13 upstanding from the rear face 14 of the backing member, that portion being connectable to a lead of an e.c.g. machine. The contact 12 extends through the centre of the backing member and includes a portion 15 exposed at front face 16 of the backing member. The front face 16 of the backing member carries an annulus 17 of adhesive material which in turn carries an annulus 18 of release paper protecting the adhesive annulus 17.

The annuli 17 and 18 surround a pad 19 of foamed plastics material which is impregnated with a silver chloride electrode gel to provide electrical contact with the skin. To minimise drying out of the gel the annulus 18 carries a cover 20 of low moisture permeability material. In use the annulus 18 together with cover 20 is peeled away from the remainder of the "electrode" and that in turn is placed on the patient's skin with the gel-impregnated pad 19 in contact with the skin. The "electrode" is held on the skin by adhesive annulus 17 and electrical connection is made via portion 13 of contact 12.

The prior art design of e.c.g. "electrode" described above has a number of disadvantages, in particular:

1. The electrode gel tends to dry out during storage which renders the "electrode" useless for monitoring purposes.

2. Drying out of the "electrode" can also create

problems after the device has been attached to the patient, causing baseline drift in the resulting e.c.g. trace and other noise problems on the signal.

3. Since they are intended to detect a small (1 to 2mV) differential voltage that is varying with the action of the heart, and because the means of obtaining electrical contact with the body uses a voltaic cell, polarisation of the "electrode" can occur with consequent loss of function.

4. Again because of the voltaic cell nature of these devices, it is hard to get pairs of "electrodes" that are perfectly matched, as they need to be in order to obtain reliable differential voltage e.c.g. traces. The output of the "electrode" depends strongly on the ionic concentration of the electrode gel (again an evaporation-related problem) and the "cell" distance through which the signal is passed.

5. For similar reasons, "electrodes" (even from the same source) are highly variable. They are furthermore very susceptible to patient movement which may alter the effective "cell" distance.

Referring to Figure 2, the e.c.g. "electrode" or transducer there shown again comprises a flexible plastics disc-shaped backing member 11 having mounted thereon at its centre a metal contact 12. Again the contact includes a stud portion 13 upstanding from the rear face 14 of the backing member which is connectable to a lead of an e.c.g. machine. At the front face 16 of the backing member 11 the stud 12 extends through the centre of the backing member and into intimate contact with a layer 26 of an adhesive and conductive composition in accordance with the invention, for example, a composition as described specifically above. The layer 26 in turn is covered by a release paper 18' e.g. a silicone release paper.

All of the layers of the transducer are co-terminous and in use the release paper 18' is removed and the transducer is adhered to the skin via layer 26. That layer being conductive as well as adhesive provides the necessary electrical contact between the lead attached to stud portion 13 and the patient's skin to which layer 26 is adhered

Another form of e.c.g. transducer in accordance with the invention is shown in Figure 3. That

transducer is similar to the transducer of Figure 2 except that the adhesive layer is carried on a support layer 25 e.g. of nylon mesh, and layer 26 comprises an annulus 27 of non-conductive adhesive material and a central plug 28 of a conductive-adhesive composition in accordance with the invention, for example, as described specifically above. The annulus 27 is preferably a hypoallergenic adhesive material, for example, as is presently used in ostomy.

It will thus be seen that the transducer of the invention can be produced in a form superficially similar to the form of known "electrodes" as shown in Figure 1. In this case, however, the electrode gel impregnated foam is replaced by a composition in accordance with the invention and the annulus 17 is selected to comprise a hypoallergenic adhesive material. In this form the transducer of the invention offers the added advantage of reduced noise to signal ratio by virtue of the reduced area of electrically-conductive material, which can act in the manner of an antenna.

The composition of the invention does not "dry out" in the same manner as a silver chloride electrode gel. Accordingly, there is no requirement for special packaging and transducers as shown in Figures 2 and 3 and as described above have an almost indefinite shelf life.

An e.c.g. transducer designed as described above offers substantial improvements over e.c.g. "electrodes" currently in use. For example, based on a commercial check-list for the ideal monitoring "electrode", a number of advantages may be noted in comparison with "electrodes" of conventional type. Thus, e.c.g. transducers in accordance with the invention:

1.<u>Require no time or education to prepare for application to the patient:</u>

The basic skin adhesive system is used by ostomates and requires only the removal of a release paper which protects the adhesive. Adhesion to skin is immediate though generally improves if pressure is sustained for a short time allowing the material to warm to body temperature and then to increase contact by flow. There is no special packaging to remove, as in the case of "electrodes" using an electrode gel, where this is required to minimise evaporation which can result in

drying out of the "electrode". The amount of preparation and training is not greater than that required for present "electrodes". Our transducer does not require any checking to see that an electrode gel pad is sufficiently moist nor, as in some cases, to add electrode gel to the pad of an "electrode" supplied in the dry state.

2.Adhere to any patient over long periods of time even though there may be heavy perspiration, showers and baths:

Clearly, in use for attaching ostomy devices to patients the need for good long term adhesion is even more stringent than those required for e.c.g. purposes. Accordingly, our system remains intact through baths and showers. Although we could not claim that this adhesive system would work with every type of skin, on the basis of the evidence from ostomy applications, there would appear to be few cases of skin types on which the system performs less well.

3.Provide a good signal immediately on application and maintain this quality throughout the use period:

Subject to what we have said above concerning light abrading of the skin, our transducers offer good immediate electrical contact and remain stable throughout their use, which contrasts with the conventional electrode gel "electrode" which requires some time to attain a thermochemical balance with the skin following application. Furthermore, with a conventional "electrode" connected into a voltage measuring circuit, the point of thermochemical balance may be shifted and again require time to restore the system to the new balance point. Once the conventional "electrode" has been applied, the electrode gel slowly dries out thus altering its response characteristics so that a slow drift in the signal can occur. These adverse effects are not possible with our transducers.

4. Provide a consistently good signal from patient to patient:

Unlike conventional electrode gel "electrodes" which, being based on a voltaic cell contact with the skin, can and do vary, our transducers offer a direct contact with the skin. They are consequently matched to each other offering more reliable results and, furthermore, do not depend significantly on the condition of the patient's

skin and perspiration (e.g. salt content).

5. Are non-irritating for extended periods of time:

While one cannot rule out the possibility that the skin of some patients might be sensitive to the adhesive system and show adverse reaction, based on use of the basic system by ostomates in a particularly sensitive (peristomal) skin area, we know of no adverse reactions from a wide variety of patients. This contrasts with the "electrodes" presently in use where adverse reactions are frequent both to the electrode gel and to the adhesive used to attach the device to the patient.

6. Are comfortable for the patient to wear:

One feature of our transducers is that they can be made with a smaller area of contact with the skin than existing electrode gel "electrodes". This is because the electrical contacting medium is itself adhesive unlike the electrode gel impregnated pad. This immediately offers improvements in patient comfort. In addition, there is no "burning" or "chilling" sensation which is often experienced by patients resulting from contact with the electrode gel. Our adhesive system rapidly adopts body temperature and is not cold to the touch.

7. May be removed quickly and discarded without cleaning the skin:

These are prime features for any adhesive system for ostomy use. While the basic skin adhesive system is resistant to becoming detached by direct pulling (thus it supports the weight of a filled ostomy collection bag) it can be peeled from the skin without discomfort and without leaving more than possibly traces of adhesive on the skin. Conventional "electrodes" are usually difficult to remove and usually require considerable skin cleaning after their removal.

8. Are low in cost:

Our transducers can be produced at a cost similar to that of present "electrodes".

Our transducers combine the good qualities of the basic skin adhesive system developed for ostomates with the superior electrical characteristics of the random conducting medium described above. In addition to the features of advantage indicated above, we note that our transducers offer a much improved stability in base line than conventional "electrodes". This results from the

fact that they are not based on a voltaic cell contact with the patient with all the consequences of this, arising, for example, from variability with patient movement, perspiration etc.

It is also the case that our transducers offer better electrical sensitivity (or gain) in the electrical signals that are the subject of measurement. The reason for this is not fully understood as yet, but undoubtedly results from the absence of a "voltaic cell damping effect" that is to be expected when measurements depend on transport of ions through solution (a slow process) rather than the motions of electrons (as in the case of conduction through metals).

The transducer described above with reference to Figure 2 can be produced by forming, e.g. by calendering, a laminate comprising a layer of conductive adhesive composition sandwiched between two layers of release paper. That laminate can then be cut into discs and adhered, by removing one layer of release paper, to the front face of a flexible polyvinylchloride disc of the same diameter having a press stud contact fitted at its centre.

With regard to the transducer of Figure 3, again a laminate is formed, but this time having an adhesive layer comprising a non-conducting adhesive material, for example, as is used in ostomy, sandwiched between a release layer and a support layer, e.g. of nylon mesh. That laminate is cut into discs, and at the centre of each disc a hole is punched of a size to accommodate the plug 28 of conductive adhesive composition. Each annulus thus produced is adhered via the support layer to the front face of a flexible polyvinylchloride disc of the same diameter as the original laminate disc, the polyvinylchloride disc again having a press stud type contact fitted at its centre. Then, the release paper is removed, the central hollow is filled, either by a hot or cold fill technique, with a measured quantity of a conductive adhesive composition in accordance with the invention, the structure is checked for electrical contact between the composition and the stud, and the whole is covered with a disc of release paper. Finally, the transducer is pressed, again either by a hot or cold technique, to complete its formation.

When a metal press-stud is used, it may be

necessary to pre-prepare or "prime" the surface e.g. of portion 15, which is in contact with the conductive adhesive composition, by applying a rough coating of conductive material e.g. conductive-epoxy or the like adhesive, to promote good adhesive bonding (and hence electrical contact) between the skin adhesive and the metal stud.

Thus, for example, a suitable conductive epoxy adhesive may be prepared from a standard, commercial, two-pack epoxy comprising epoxy resin and diamine curing agent such as:

(i) Araldite, or
(ii) Bostik

and these may be of either the slow set (about 12 to about 24 hours) or quick set (about 1 hour) variety. In either case, the commercial product comprises two components which are mixed together (usually in equal proportions) just prior to use. After the components are mixed, the setting process begins and the material can be used only until it has set to the extent that it is unworkable.

For use as a "primer" for the stud surface, each of the two components in a commercial product is separately mixed with silver-coated glass spheres (prepared as described above), or the like; the optimum formulation being:

Epoxy Component about 25% by weight
Silver-coated glass spheres about 75% by weight,

although the range of from about 70 to about 80% by weight of silver-coated glass spheres or the like to about 30 from about 20% by weight of epoxy component is acceptable for both of the epoxy components.

In each case, the epoxy component should be warmed e.g. to from about 40 to about 80°C, to make mixing easier, and the silver spheres added slowly while gently stirring the mixture. After a period of final mixing to ensure homogeneity, the material is cooled and then checked for electrical conductivity.

Once mixed, the two conductive epoxy components can be stored indefinitely as long as they are separate. For use, the same procedure as with the commercial epoxy adhesive is followed, that is the two components are mixed in equal proportions and the mixture worked onto the stud surface before it sets sufficiently to prevent

flow.

The transducers described above with reference to Figures 2 and 3 may be used in the usual e.c.g. applications. In those applications a set of transducers is attached to various parts of the body and each is separately connected to an e.c.g. apparatus. A commonly used arrangement uses three transducers arranged on the chest or limbs in a so-called Eindhoven triangle, for example, with a measuring transducer on the right arm (RA), a measuring transducer on the left arm (LA), and a measuring transducer on the left leg (LL). A set of three voltages is monitored i.e. between each pair of transducers using a differential amplifier, working in the 1 to 2 millivolt range at low current, the third transducer in each case providing a ground connection. On some occasions a fourth transducer is used connected say to the right leg (RL) to provide a separate means of grounding the patient on a common line with the measuring instrument.

Other arrangements use additional transducers mounted singly or in clusters at other parts of the body, particularly near the heart. Thus, sometimes in these cases a cluster of seven or nine transducers is placed near the heart and this presents a problem in siting the various transducers close enough together. While this problem is partially alleviated by producing transducers as described above with reference to Figures 2 and 3 of a size smaller than that of the conventional "electrode", which can be done because the whole of the face area is adhesive, better results can be obtained by constructing a device of the type illustrated in Figure 4.

Figure 4 shows a multiple contact transducer in which the face shown is constructed as a series of portions or plugs 31 of a conductive-adhesive composition in accordance with the invention, for example, as described specifically above, disposed in an arcuate array in a facing element 32 comprising hypoallergenic skin adhesive material as described above. The whole is carried on a suitable structure, for example, a similarly-shaped polyvinylchloride backing sheet carrying press stud contacts at the appropriate locations for each of the plugs 31.

The above transducer provides a means of obtaining

multiple transducer contact points where an array of independent transducers around the heart is required.

It is to be understood that the present invention is not limited to the specific embodiments described above. Thus, for example, the formable composition of the invention may be used in the following alternative applications:

1. A stud or a combined backing member and stud can be formed for use in the e.c.g. transducer described above. This could replace the metal press stud and/or combine it with the p.v.c. backing disc. In either case the unit could be produced by forming e.g. by injection moulding, a polymer composition comprising p.v.c., nylon, polypropylene or like material and metal or metal-coated particles, e.g. silver-coated glass spheres.

2. Metal-coated glass fibre-filled polypropylene may be employed for injection moulded applications, of which conductive model railway wheels is one example. At present these are produced from glass fibre-filled polypropylene (for strength) and require that a metal insert "spoke" is incorporated into the injection mould before forming each wheel so as to permit transfer of current from the rim of the wheel to the hub and thence to a drive motor. Our solution to the problem would greatly simplify the construction process by offering a conductive composition from which a wheel can be formed.

3. Extruded coaxial type cable, especially for use in high quality signal transmission, e.g. hi-fi, computers, television, etc. At present such cables have a wire centre onto which is extruded an insulating polymer. This is then wire wrapped using woven wire along its length (the earthing or screening layer) and then a final polymer layer is extruded onto this. The main disadvantages are the complexity of the forming process and the inefficiency of the grounding woven wire layer which has to be woven to give flexibility, but then offers inefficient electrical screening. Our proposal is to replace both of the metal layers by a conductive polymer. This can be achieved by co-extrusion processes which are much simpler than the present methods. Furthermore, the screening layer is then more efficient by virtue of providing an essentially complete layer of conducting material.

4. Conductive polymer foams. By incorporating metal or metal-coated particles into a polymer (e.g. polyurethane) which is then subjected to foaming, we attain a conductive foam which has applications in low static packaging and for the protection/screening of electrical components.

5. Injection-moulded "printed circuit" boards for electrical equipment. Where an electronic circuit is standard, and thus produced in quantity, so that it is worthwhile designing a mould, a combination of conductive and non-conductive polymers can be injection-moulded to provide preformed circuit boards more efficiently than by present techniques.

6. Conductive rubber (or similar material) pressure transducers. By incorporating conductive particles into a rubber material exactly at the critical percolation volume, we can obtain a material whose conductivity changes markedly on compression and reversibly on decompression (because of rubber recovery). This offers a means of providing pressure control in electrical circuitry, for example, in foot-operated control circuits such as sewing machines. It is to be understood, of course, that such materials would have a conductivity far in excess of that of graphite filled rubber, for example, by a factor of about 100.

7. Injection-moulded television aerials.

8. "Cold solder" or two-pack electrically-conductive adhesive for metals. Such a material could be formulated as described above for the epoxy metal stud "primer" and could find application in the joining of two metallic components where a conductive join is required.

CLAIMS

1. A formable polymer composition, which composition comprises a formable polymeric material having dispersed therein an electrically-conductive material in particulate form comprising metal or metal-coated particles, the conductive material being present in an amount to provide an overall specific conductivity of at least about 2 mho cm^{-1}.

2. A composition according to claim 1, wherein the polymeric material is a polyvinyl compound, a polyalkene, a polyacrylate, a polymethacrylate or a polyamide.

3. A composition according to claim 2, wherein the polymeric material is a polyvinylchloride, a polyethylene, a polypropylene, a polyisobutene or a nylon.

4. A composition according to claim 1, wherein the polymeric material is an epoxy resin or a silicone.

5. A composition according to any one of the preceding claims, wherein the electrically-conductive material comprises a particulate metal.

6. A composition according to any one of claims 1 to 4, wherein the electrically-conductive material comprises substrate particles coated with a film of metal.

7. A composition according to claim 6, wherein the substrate is glass or a plastics material.

8. A composition according to any one of the preceding claims, wherein the metal is silver.

9. A composition according to any one of the preceding claims, wherein the particulate form of the electrically-conductive material is spherical.

10. A composition according to claim 9, wherein the particles of electrically-conductive material are spheres of narrow diameter distribution which are present in an amount in excess of about 35%.

11. A composition according to any one of claims 1 to 8, wherein the particulate form of the electrically-conductive material is elongate with a high length to diameter ratio.

12. A composition according to claim 10, wherein the

particles are rods or fibres.

13. A composition according to any one of the preceding claims, which includes one or more components to provide a composition having contact adhesive properties.

14. A composition according to any one of the preceding claims, wherein its components are selected so as to provide a hypoallergenic composition.

15. A composition according to claim 13 or claim 13 and claim 14, wherein adhesivity is provided by employing a mixture of a polyisobutene together with one or more phase structure, flow and/or moisture permeability modifiers.

16. A composition according to claim 15, wherein the polyisobutene is one having a viscosity average molecular weight of from about 40,000 to about 100,000.

17. A composition according to claim 15 or claim 16, which includes one or more low molecular weight polyalkenes and/or hydroxyalkylcelluloses.

18. A composition according to claim 17, which includes polyethylene and/or hydroxymethylcellulose.

19. A composition according to any one of claims 13 to 18, which includes an additive to reduce contact resistance with skin when applied to unprepared skin.

20. A composition according to claim 19, wherein the additive comprises a mixture of water, a hygroscopic agent and a thickening agent.

21. A composition according to claim 20, wherein the hygroscopic agent is glycerine or glycerol and/or the thickening agent is carboxymethylcellulose.

22. A composition according to any one of claims 19 to 21, which is formulated by preparing a first mixture comprising the said additive and the said electrically-conductive material, and a second mixture comprising the said polymeric material and the said electrically-conductive material, those mixtures then being blended to form the final composition.

23. A composition according to claim 22, wherein in the first mixture there is employed a ratio of hygroscopic agent to water of from about 20:80 to about80:20 by weight, a proportion of thickening agent to hygroscopic agent/water mixture of from about 2% to about 10% by weight, and a proportion of electrically-conductive material, in the overall mixture, of from

about 70% to about 80% by weight.

24. A composition according to claim 22 or claim 23, wherein the first mixture is employed in an amount of no more than about 15% by weight based on the total weight of the composition.

25. A composition according to claim 1 or claim 13 substantially as hereinbefore described specifically.

26. An electrically-conductive device for medical purposes, which device comprises one or more formed portions of a composition according to any one of the preceding claims, if desired supported on a substrate structure.

27. A device according to claim 26, which is a transducer suitable for use in electrocardialogical applications, the transducer comprising a backing member through which is mounted an electrically-conductive contact whereby an electrical lead can be connected to one part of the contact at the rear of the backing member and the contact provides an unbroken electrical path through the backing member to a portion of an electrically-conductive adhesive composition according to claim 13 or any one of claims 14 to 25 when dependent on claim 13 forming at least part of an adhesive layer disposed on the front of the backing member whereby the front of the transducer may be adhered to the skin.

28. A device according to claim 27, wherein the electrically-conductive contact is a stud formed of metal of a formable composition according to any one of claims 1 to 12.

29. A device according to claim 27 or claim 28, wherein the contact is mounted at the centre of the backing member.

30. A device according to any one of claims 27 to 29, wherein the backing member is a disc.

31. A device according to claim 29 and claim 30, wherein the front surface of the backing member bears an annulus of non-conducting contact adhesive material surrounding a central portion or plug of said electrically-conductive adhesive composition.

32. A device according to claim 31, wherein the annulus comprises a hypoallergenic pressure-sensitive skin adhesive.

33. A device according to claim 26, which is a multiple-contact transducer, which comprises an array of

electrically-conductive portions carried on an insulating backing member, each portion being in electrical contact with an isolated terminal, and at least one portion comprising an electrically-conductive adhesive composition according to claim 13 or any one of claims 14 to 25 when dependent on claim 13.

34. A device according to claim 33, wherein each electrically-conductive portion comprises said electrically-conductive adhesive composition.

35. A device according to claim 33 or claim 34, wherein the electrically-conductive portions are disposed on the backing member in an arcuate array for attaching to a patient's chest around the heart.

36. A transducer substantially as hereinbefore described with reference to and as illustrated in any one of Figures 2, 3 or 4 of the accompanying drawings.

37. A method of manufacturing a device according to claim 27, which method comprises:
(a) forming a sheet of a laminate comprising a layer of a composition according to claim 13 or any one of claims 14 to 25 when dependent on claim 13 sandwiched between two release layers,
(b) sub-dividing the laminate into transducer elements,
(c) removing one release layer, and
(d) adhering each element via its exposed adhesive face to a backing element including an electrically-conductive contact which provides an unbroken electrical path through the backing member to the conductive composition.

38. A method according to claim 37, wherein the laminate is cut into discs.

39. A method according to claim 37 substantially as hereinbefore described specifically.

40. A method of manufacturing an electrode according to claim 31 or claim 33, which method comprises:
(i) forming a sheet of laminate comprising a layer of a non-conductive contact adhesive composition sandwiched between a release layer and a supporting layer,
(ii) sub-dividing the laminate into transducer elements,
(iii) providing at least one aperture through each element,
(iv) adhering each element via its supporting layer to a backing element including an electrically-conductive contact which provides an unbroken electrical path

through the backing member to the or each aperture.
(v) removing the release layer,
(vi) filling at least one aperture with a portion of a composition according to claim 13 or any one of claims 14 to 25 when dependent on claim 13, and
(vii) covering the front adhesive face with a release layer.

41. A method according to claim 40, wherein the transducer elements are discs and the apertures are essentially round in plan.

42. A method according to claim 40, wherein the transducer elements are horse-shoe shaped.

43. A method according to claim 42, wherein at least three apertures are provided.

44. A method according to claim 40 substantially as hereinbefore described specifically.

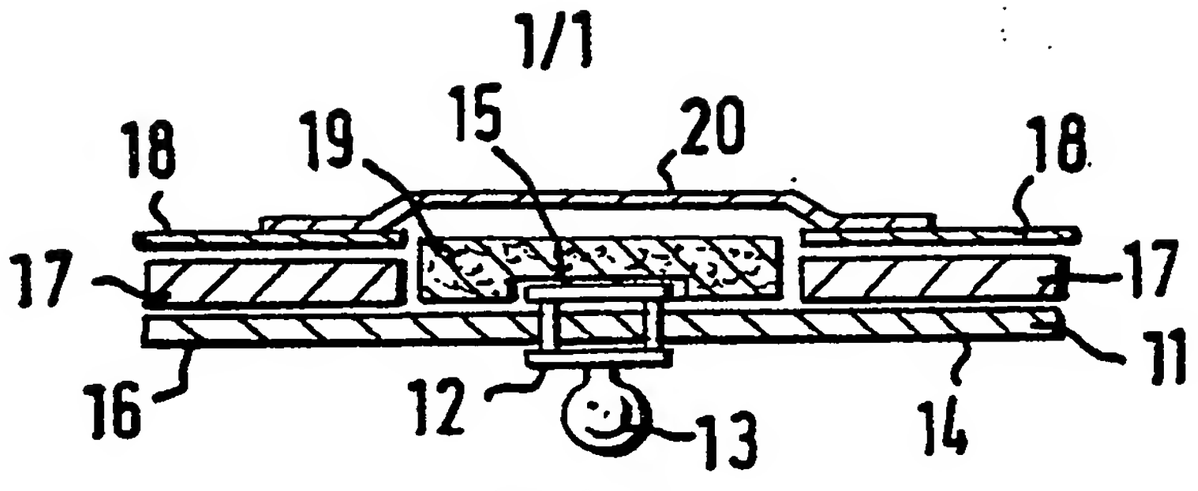

FIG.1

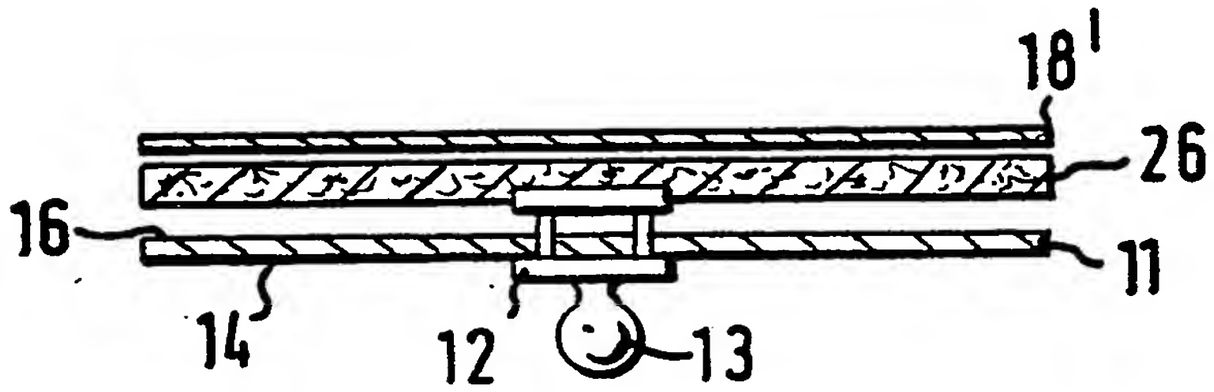

FIG.2

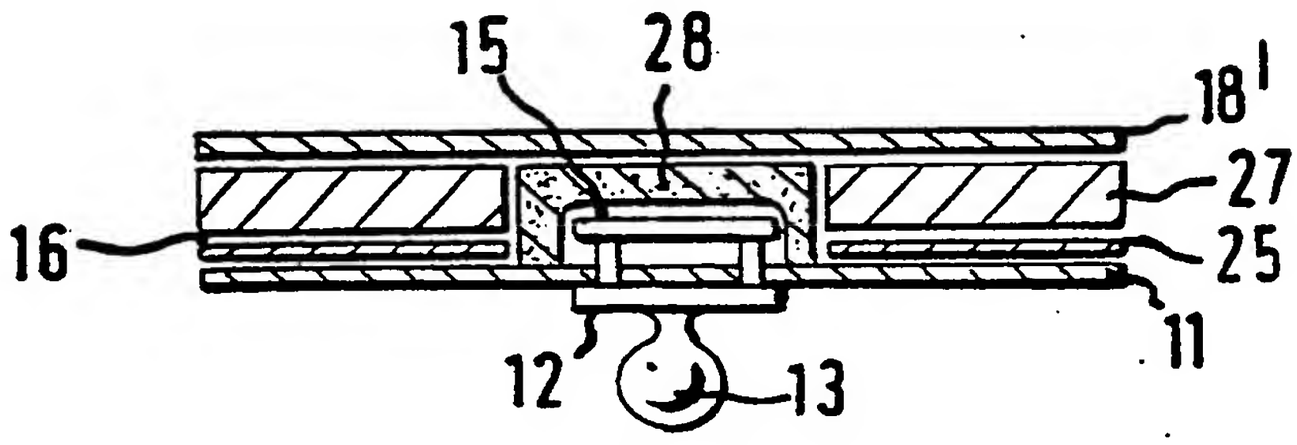

FIG.3

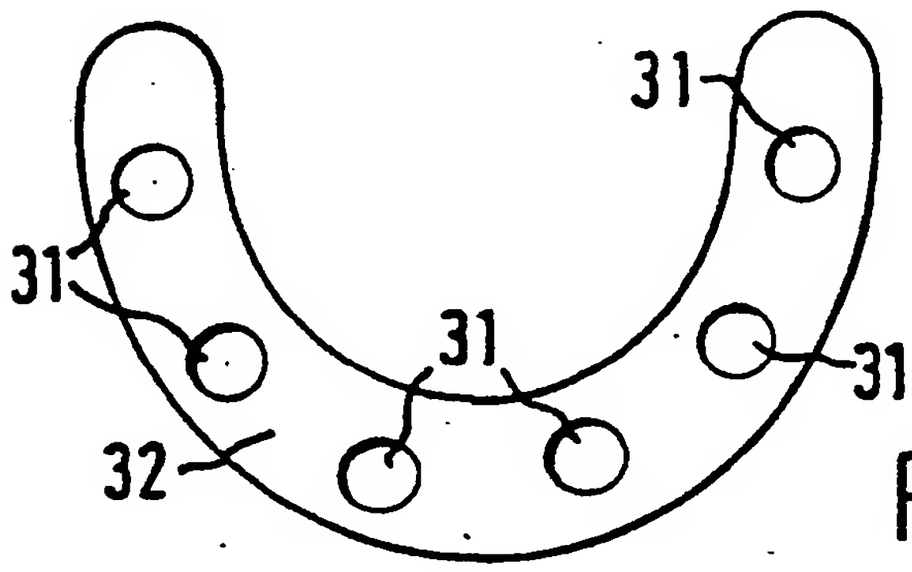

FIG.4

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 83/00328

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [2]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[3]: H 01 B 1/22

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC[3]	H 01 B 1/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 3746662 (R.L. ADELMAN) 17 July 1973 see column 1, lines 70-72; column 2, lines 1-9 and 13-30; column 4, lines 69-73; column 5, lines 3-10; claims 1-19	1,4-7,9,11
X	FR, A, 1533642 (HYSOL) 19 July 1968 see example 7; claims 1-10	1,4,5,8
X	US, A, 4098945 (R.W. OEHMKE) 4 July 1978 see column 1, lines 43-47; column 3, lines 57-66; column 7, lines 8-30; claims 1-12	1,2,5-8,10, 13
X	EP, A, 0059456 (DIAMOND SHAMROCK) 8 September 1982 see page 8, lines 11-30; page 9, lines 13-35; claims 1-18	1,3,4,6,7, 11
A	US, A, 3983075 (D.W. MARSHALL et al.) 28 September 1976 see column 7, lines 57-61; claims 1-7	1,4

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [1]	Date of Mailing of this International Search Report [2]
7th March 1984	18 AVR. 1984
International Searching Authority [1]	**Signature of Authorized Officer** [10]
EUROPEAN PATENT OFFICE	G.L.M. Kruydenberg

Form PCT/ISA/210 (second sheet) (October 1981)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 83/00328 (SA 6215)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 06/04/84

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3746662	17/07/73	None	
FR-A- 1533642		NL-A- 6710753	06/02/68
		GB-A- 1189199	22/04/70
US-A- 4098945	04/07/78	None	
EP-A- 0059456	08/09/82	JP-A- 57165444	12/10/82
		AU-A- 8078682	02/09/82
US-A- 3983075	28/09/76	US-A- 4071737	31/01/78